A structural consideration of kanemite, octosilicate, magadiite and kenyaite

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By comparing data from ^{29}Si, ^{1}H and ^{23}Na NMR studies, new model structures have been proposed for the layered sodium polysilicate hydrates, kanemite, octosilicate, magadiite and kenyaite. These are based on the known structures of the anhydrous silicate, $KHSi_2O_5$, and piperazine silicate (EU19), rather than the known structure of the layered sodium polysilicate hydrate, makatite, which previous authors have used as a basis for their models.

Makatite, kanemite, octosilicate, magadiite and kenyaite form a series of sodium polysilicate hydrates with formulae, $Na_2O{\cdot}(4\text{–}22)SiO_2{\cdot}(5\text{–}10)H_2O$.[1] Their physical properties include a high capacity for ion exchange, whereby sodium ions can be replaced by protons, other cations or large quaternary ammonium ions. With the availability of many facile synthetic routes,[2] they are potentially valuable in catalyst or detergent systems.

Only the structure of makatite is known.[3] In simple terms, it consists of silicate layers, separated by hydrated sodium ions, and a schematic diagram is shown in Fig. 1. Powder X-ray diffraction suggests that this is also a reasonable model for the other four silicates, giving a value for the basal spacing in each case from a strong reflection at a low value of 2θ. It can be concluded from Table 1, which lists typical formulae and basal spacings, that the silicate layers become thicker in going from makatite to kenyaite. This can be related to an increase in condensation, confirmed by ^{29}Si NMR studies, which quantify the types of silicon species present in terms of their connectivity: Q^3, $(SiO)_3\mathbf{Si}{-}O^-$, and Q^4, $(SiO)_4\mathbf{Si}$. The relative proportions of Q^3 and Q^4 silicon atoms (the only ones present in these silicates) are also shown in Table 1. It should be noted that the formulae given for the layer silicates are idealised. Actual contents show some variation, especially for magadiite and kenyaite.[12] Such variations influence the apparent $Q^3:Q^4$ ratio.[13]

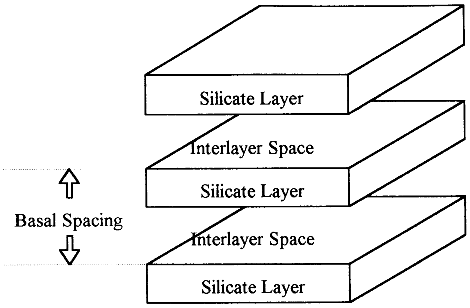

Fig. 1 A schematic diagram of the structure of makatite, and, equally, kanemite, octosilicate, magadiite and kenyaite: two-dimensionally infinite silicate layers, separated by interlayer spaces

Table 1 Formulae and structural details for five layered sodium polysilicate hydrates (basal spacing values are obtained from powder X-ray diffraction and $Q^3:Q^4$ ratios come from solid-state ^{29}Si NMR studies)

silicate	formula[a]	basal spacing[b] /Å	connectivity ratio, $Q^3:Q^4$
makatite	$Na_2O{\cdot}4SiO_2{\cdot}5H_2O$	9.03	1:0
kanemite	$Na_2O{\cdot}4SiO_2{\cdot}7H_2O$	10.3	1:0
octosilicate	$Na_2O{\cdot}8SiO_2{\cdot}9H_2O$	11.0	1:1[c]
magadiite	$Na_2O{\cdot}14SiO_2{\cdot}10H_2O$	15.6	1:3[d]
kenyaite	$Na_2O{\cdot}22SiO_2{\cdot}10H_2O$	20.0	unknown[e]

[a]Ref. 1. [b]Ref. 2, 4–7. [c]An undisputed value, confirmed from unsaturated spectra by Hauck.[8] [d]Conflicting values have been reported, but when T_1^{Si} is considered this is the only result, first reported by Dailey and Pinnavaia,[9] confirmed by Heidemann.[10] [e]Again conflicting values have been reported. Our studies indicate a value of 1:5.[11]

Hypothetical structures have been proposed for octosilicate, magadiite and kenyaite which are based on the condensation of individual makatite layers.[1,4] Schwieger *et al.*[4] used the connectivity ratios observed from ^{29}Si NMR studies ($Q^3:Q^4=1:1$, $1:2$ and $1:4$, respectively) to link the makatite sheets. Although the resulting structures could be used to explain the thermal properties of these silicates, they were inconsistent with observed basal spacings obtained by powder X-ray diffraction. Nesbitt[1] also used the condensation of makatite sheets to generate models for the more siliceous silicates, and noticed that individual sheets could be combined in two ways. These models incorporated Q^3 sites within the layers which appeared to be consistent with ^{23}Na CP NMR spectra (suggesting the presence of isolated sodium ions in magadiite and kenyaite).[1,14] However, more recent ^{23}Na NMR studies have shown that the ^{23}Na signal in question (at $\delta_{Na}\approx 7$) probably comes from sodium chloride contamination in the samples.[15] These models are also inconsistent with the X-ray data. The models derived from makatite layer condensations are shown in Fig. 2. Pinnavaia *et al.*[16] proposed an alternative model for magadiite based on NMR data. This gave the correct basal spacing, but was inconsistent with the chemical composition.[17] Brandt *et al.*[17] highlighted these problems and proposed a refinement of the Schwieger *et al.*[4] models, in which the SiO_4 tetrahedra heights in the silicate sheets were reduced to a minimum. The resulting models had basal spacings in much better agreement with the experimental findings. The more recent studies[15] suggested to us that the interlayer structure of makatite is very different from that of the more siliceous silicates, and that the makatite layer may be an inappropriate building unit for structural models of these materials. Almond *et al.*[18] drew attention to the apparently corresponding hydrogen-bonding situation between kanemite and the anhydrous silicate, $KHSi_2O_5$, which like makatite contains only Q^3 silicon atoms, and Apperley *et al.*[5] went on to propose that the kanemite structure is based on that of $KHSi_2O_5$.

In this work, new structural conclusions for kanemite, octosilicate, magadiite and kenyaite will be proposed from comparisons of their NMR spectra with those of makatite, $KHSi_2O_5$ and of piperazine silicate (EU19).[19,20]

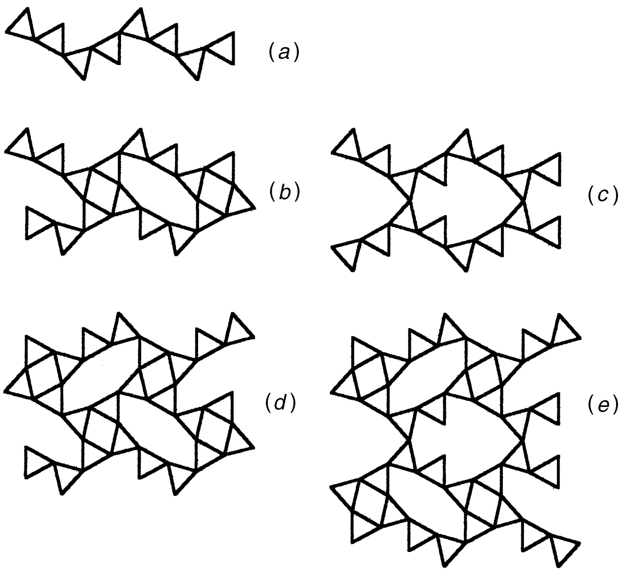

Fig. 2 The condensation of makatite to form thicker silicate layers. (*a*) A silicate layer of makatite, the projection along *a*, [as with Fig 4(*a*) later]. (*b*) Two makatite layers may be condensed to form a double layer separated by four- and eight-membered rings. (*c*) Alternatively, two makatite layers may be condensed to give a double layer separated by ten-membered rings. (*d*) The magadiite model of Schwieger *et al.*,[4] three makatite layers condensed according to the method shown in (*b*). (*e*) The magadiite model of Nesbitt,[1] four makatite layers condensed according to the methods of (*b*) and (*c*).

Structures of makatite, $KHSi_2O_5$ and piperazine silicate (EU19)

Structures of makatite, $KHSi_2O_5$ and piperazine silicate (EU19) have been resolved by diffraction techniques and reported by Annehed *et al.*,[3] Le Bihan *et al.*[21] and Andrews *et al.*[20] Makatite and $KHSi_2O_5$ are single-sheet silicates where each sheet is made up of a slightly different arrangement of six-membered rings of silicon atoms, as shown in Fig. 3. They also differ in their interlayer species. Fig. 4 shows that the silicate layers in makatite are separated by hydrated sodium ions, whereas there are interlayer hydrogen bonds and potassium ions between the silicate layers of $KHSi_2O_5$. The structure of EU19 consists of double silicate layers of eight-membered rings [Fig. 5(*a*)], linked by five-membered rings [Fig. 5(*b*)], and contains silicon atoms of both the Q^3 and Q^4 types. The double layers are held together by hydrogen bonds with piperazinium cations.

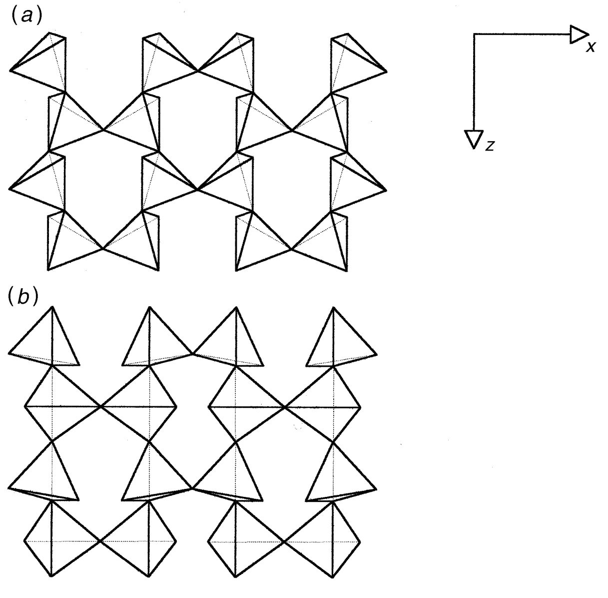

Fig. 3 Silicate layers containing six-membered rings of silicon atoms: (*a*) $KHSi_2O_5$;[21] (*b*) makatite.[3] In each case the tetrahedra represent SiO_4.

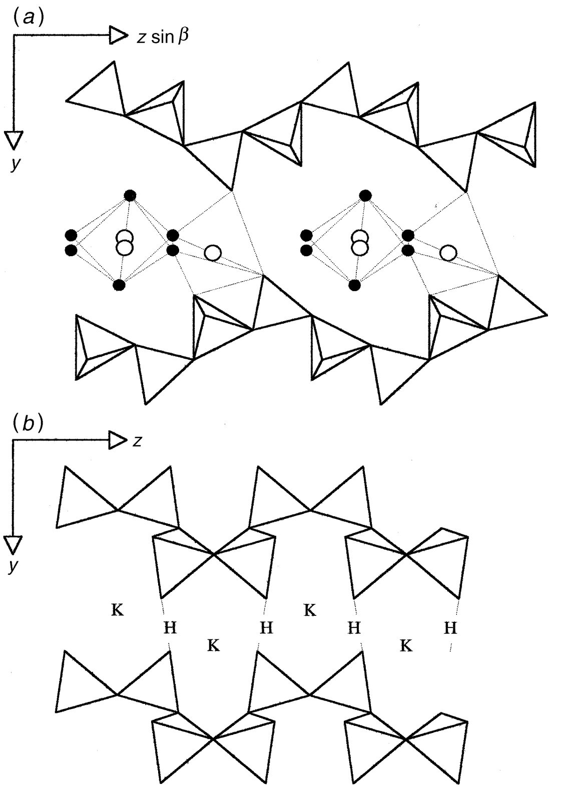

Fig. 4 Schematic diagrams showing layer structures. (*a*) Makatite, showing SiO_4 tetrahedra, water oxygen atoms (small filled circles) and sodium ions (large unfilled circles). According to the notation of Annehed *et al.*,[3] this is a projection along *a*. (*b*) $KHSi_2O_5$, showing potassium ions, hydrogen bonds, SiO_4 tetrahedra and SiO_3 triangles (one oxygen atom not shown for clarity, as in this view it coincides with another oxygen atom). According to the notation of Apperley *et al.*,[5] this is a projection along the *z* axis.

Experimental

The makatite and octosilicate samples used in this work were obtained from a variety of sources, while piperazine silicate (EU19) was prepared according to published methods.[19] The integrity of the samples was checked by powder X-ray diffraction, using a Phillips PW1050 powder diffractometer. Some ^1H NMR results were confirmed by thermogravimetry, heating a small sample to *ca.* 800 °C over 2–3 h. NMR spectra were acquired with Chemagnetics CMX200 and Varian Unity Plus 300 spectrometers using standard Chemagnetics or Doty probes and conventional single-pulse or cross-polarisation pulse sequences. The spectrometer frequencies used were 39.76 and 59.58 MHz for ^{29}Si and 200.13 and 299.95 MHz for ^1H. The chemical shifts were referenced to tetramethylsilane, while Hartmann–Hahn matching conditions for ^{29}Si cross-polarisation were set using tetra(*tert*-butyl)silane or tetrakis(trimethylsilyl)silane. All NMR measurements were carried out at ambient probe temperature.

Results

^{29}Si NMR

Table 2 reviews ^{29}Si NMR data on the five layered sodium polysilicate hydrates, piperazine silicate (EU19) and $KHSi_2O_5$. Many authors have reported ^{29}Si NMR spectra for kanemite, magadiite, kenyaite and $KHSi_2O_5$; typical values are quoted

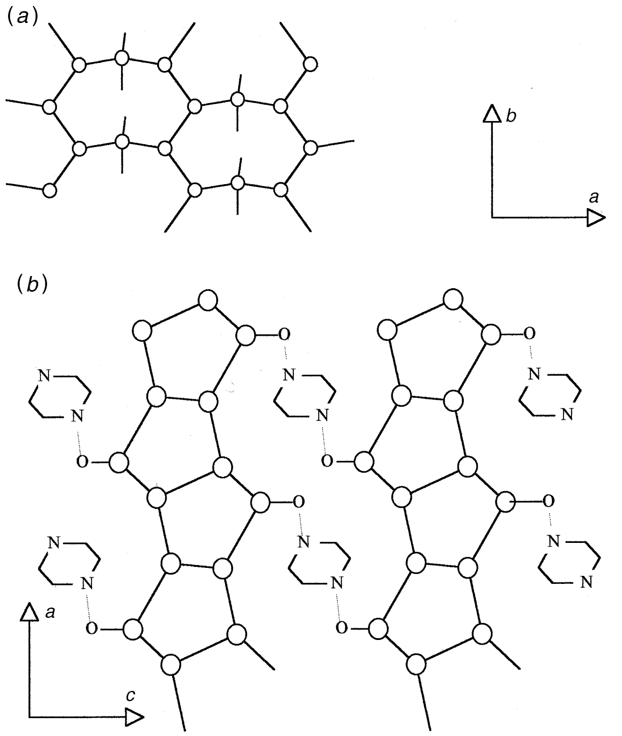

Fig. 5 The structure of piperazine silicate (EU19):[20] (*a*) a component of the double silicate layer in projection along *c*; and (*b*) a *b* axis view, showing double silicate layers held together by hydrogen-bonding interactions with piperazinium cations. In each diagram, circles represent silicon atoms; these are separated by oxygen atoms (not shown).

Table 2 The number of signals observed in ^{29}Si NMR spectra of the five layered sodium polysilicate hydrates, $KHSi_2O_5$ and piperazine silicate (EU19)

	number of signals		
silicate	Q^3	Q^4	ref.
makatite	4	0	this work
kanemite	1	0	Apperley *et al.*[5]
octosilicate	1	1	this work
magadiite	1	3	Dailey and Pinnavaia[9]
kenyaite	1	many	Nesbitt[1]
$KHSi_2O_5$	1	0	Deng *et al.*[22]
EU19	1	2	this work

for these. The literature contains only a single makatite ^{29}Si spectrum for an obviously contaminated sample.[23] In this work, the high-resolution spectrum shown in Fig. 6 will be considered. Fig. 6 also contains the first reported spectrum of EU19 and a typical spectrum of octosilicate, for comparison.

The makatite spectrum has four resolved lines over a range of less than 2 ppm, assigned to silicon atoms of type Q^3. The unit cell of makatite contains four silicon atoms, so each signal can be assigned to one of these. In the unit cell, the silicon atoms differ in two ways. First, there are small differences in parameters such as average Si—O—Si bond angle and Si—O bond length, which have been shown to correlate with δ_{Si}.[24] These could explain small differences in chemical shift. Secondly, and more profoundly, there is a difference in the association with the interlayer sodium ions. In the unit cell, three of the silicon atoms are bonded to oxygen atoms which form part of the sodium coordination sphere. These can be considered to be more siloxide, ≡Si—ONa, in nature than the other silicon atom, which according to the stoichiometry of the system would be better described as silanol, ≡**Si**—OH. (Relative terms have been used because it would be incorrect to refer to three siloxide silicon atoms and a single silanol in

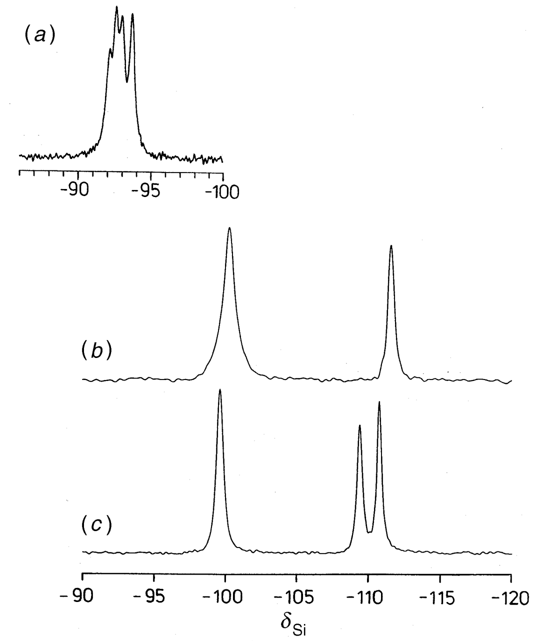

Fig. 6 ^{29}Si CP MAS NMR spectra of: (*a*) makatite (59.58 MHz, 48 transients, 10 s recycle time, 3 ms contact time and 3.5 kHz spinning rate); (*b*) octosilicate (39.76 MHz, 800 transients, 2 s recycle time, 2 ms contact time and 2 kHz spinning rate); and (*c*) piperazine silicate (EU19) (39.76 MHz, 256 transients, 10 s recycle time, 5 ms contact time and 1.97 kHz spinning rate)

a system which, according to the formula of makatite, should have two of each.)

The unit cell of $KHSi_2O_5$ has a single type of silicon atom, which is observed in the ^{29}Si spectrum. There are no siloxide and silanol silicon atoms here because of hydrogen bonding and we see a single type, ≡**Si**—O···H. The unit cell of EU19 contains three silicon atoms, numbered Si-1, Si-2 and Si-3.[20] These are of type Q^4, Q^3 and Q^4 respectively. This conforms with the ^{29}Si spectrum which shows one Q^3 signal at δ_{Si} −99, and two Q^4 at δ_{Si} −109 and −111. Again, hydrogen bonding means we only see one type of Q^3 silicon atom, ≡**Si**—O···[piperazinium]$^{2+}$. The two Q^4 sites differ significantly in their average Si—O—Si bond angles, θ: for Si-1, $\theta = 145.3°$; and for Si-3, $\theta = 150.85°$. Smith and Blackwell have shown that there is a good correlation between the silicon chemical shift and the average Si—O—Si bond angle.[24] Their empirical equation, $\sec\theta = -3.1571 - 0.017847\delta_{Si}$, predicts chemical shifts of δ −108.7 (Si-1) and −112.7 (Si-3) from the unit cell data. This is an adequate difference for the full assignment of the ^{29}Si spectrum of EU19 with the three signals at δ_{Si} −99, −109 and −111 corresponding to Si-2, Si-1 and Si-3, respectively.

With kanemite, octosilicate, magadiite and kenyaite, we see only one Q^3 signal in the ^{29}Si NMR spectra. This is an important result when the stoichiometry of the silicates is considered. The formulae of kanemite, octosilicate, magadiite and kenyaite can be written in the form $Na_2H_2Si_xO_{2x+2}\cdot yH_2O$, where $x = 4$, 8, 14 and 22, respectively and $y = 6$, 8, 9 and 9, respectively. Therefore, in each silicate, there are equal numbers of sodium ions and protons to counter the charge on the oxygen atom of a Q^3 silicon atom, ≡Si—**O**$^-$. Structurally, these can be accommodated by the presence of silanol and siloxide silicon atoms, as in makatite, or with hydrogen bonds between the Q^3 silicon atoms, as in $KHSi_2O_5$. Since there is only one Q^3 signal in the ^{29}Si NMR spectra of kanemite, octosilicate, magadiite and kenyaite, it is unlikely that the structures contain distinguishable siloxide and silanol Q^3 silicon atoms: the two species would not be expected to have overlapping ^{29}Si NMR signals [a semi-empirical study[25] predicts a difference in chemical shift of 3.5 ppm between $(SiO)_3\mathbf{Si}ONa$ and $(SiO)_3\mathbf{Si}OH$], especially with lines as sharp as those observed in the octosilicate spectrum of Fig. 6(*b*). The single signal in each of these spectra implies that there are hydrogen bonds between the Q^3 silicon atoms of the silicates.

^{1}H NMR

Though they have not been directly observed by X-ray diffraction methods, the known crystal structure of makatite[3] does contain two types of proton. Since there are only two sodium ions for every four siloxide oxygen atom, silanol protons, $\equiv Si-O\mathbf{H}$, must be present; water protons, $\mathbf{H}_2O$, are indicated by isolated oxygen atoms. The structure of $KHSi_2O_5$[21] contains strongly hydrogen-bonded silanol protons, $\equiv Si-O\cdots\mathbf{H}\cdots O-Si\equiv$. These three types of proton can be identified in silicates using ^{1}H MAS NMR spectroscopy. Yesinowski *et al.* studied a range of silicates, reporting a water signal at δ_H 3.1 and isolated silanol signals between δ_H 0.7 and δ_H 4.3.[26] The extent of any spinning side bands allows discrimination between the potentially overlapping lines for a firm assignment. Signals for strongly hydrogen-bonded protons come at significantly higher frequencies, such as the value of δ_H 15.8 observed in pectolite.[26] Deng *et al.* showed that the ^{1}H MAS NMR spectrum of $KHSi_2O_5$ does contain a hydrogen-bonding signal at δ_H 15.58.[22] Fig. 7(*a*) shows that there is no high-frequency signal in the ^{1}H MAS spectrum of makatite, just a single signal at δ_H 5.8 corresponding to water and silanol protons, which could not be resolved over the timescale of the NMR experiment (because of rapid chemical exchange or spin-diffusion).

Fig. 7(*b*) shows the ^{1}H MAS NMR spectrum of octosilicate. Apart from a small background signal at δ_H *ca.* 1, it consists of isotropic lines at δ_H 16.0 and 3.6 and their spinning side-bands. The chemical shift of the δ_H 3.6 peak is uninformative, since water and isolated silanol proton signals have been reported with this value. However, the spinning side-band manifold is typical of water protons in silicates.[26,27] The side-bands probably arise principally from partially averaged homonuclear dipole–dipole interactions. They extend over 15–20 kHz, significantly less than expected for rigid water molecules. Though homogeneous broadening might be expected from these interactions, spinning side-bands are seen at modest spin rates (such as were used for this work) when the water molecules are significantly mobile over the NMR timescale. The δ_H 16.0 peak can be assigned to a strongly hydrogen-bonded proton. The chemical shift can be related to the oxygen–oxygen distance of the $-O\cdots H\cdots O-$ bond, *d*, by use of an empirical equation derived by Eckert *et al.*:[27] $\delta_H = 79.05 - 0.255\,d/\text{pm}$: for $\delta_H = 16.0$, $d = 247$ pm. The narrow spread of spinning side-bands that surrounds this signal is typical of a silicate silanol proton, where chemical shift anisotropy is likely to be the dominant broadening factor. Physically, these protons are surrounded by water molecules. Therefore, broad lines might be expected in a ^{1}H MAS spectrum, from homogeneous homonuclear interactions. The sharp lines mean that the water molecules must be mobile with respect to the hydrogen-bonding protons, but not rapidly exchanging with them (since separate signals are seen).

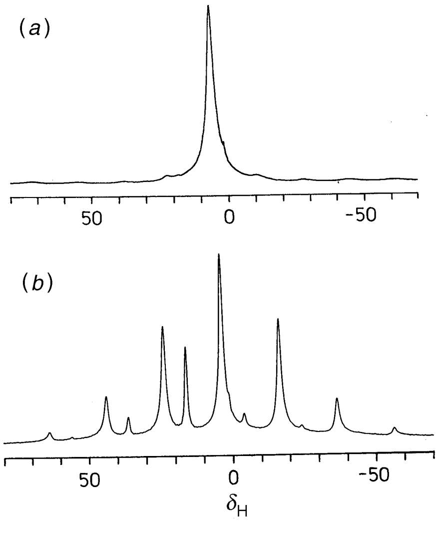

Fig. 7 ^{1}H single-pulse MAS NMR spectra: (*a*) makatite at 299.49 MHz (1000 transients, 0.5 s recycle time and 4.9 kHz spinning rate); (*b*) undried octosilicate at 200.13 MHz (32 transients, 2 s recycle time and 4 kHz spinning rate)

The ratio of hydrogen-bonded silanol and water protons is observed to be 1 : 8 in ^{1}H MAS spectra of this sample (most clearly at higher spinning rates than 4 kHz). This is consistent with the formula $Na_2H_2Si_8O_{18}{\cdot}8H_2O$ for octosilicate. This stoichiometry was confirmed by thermogravimetry. The sample of octosilicate lost 23% of its mass on heating to 800 °C (theoretical value for $Na_2O{\cdot}8SiO_2{\cdot}9H_2O = 23.0\%$). Of this, 20% was lost below 300 °C as discrete events [the proportion of $Na_2(H_{silanol})_2Si_8O_{18}{\cdot}8(H_{water})_2O$ as $(H_{water})_2O = 20.4\%$], and 3% was lost steadily above 300 °C, with no discernible event in the differential plot [the proportion of $Na_2(H_{silanol})_2Si_8O_{18}{\cdot}8(H_{water})_2O$ as $(H_{silanol})_2O = 2.6\%$]. A series of ^{29}Si and ^{23}Na cross-polarisation experiments indicated that the silicon atoms, sodium ions and hydrogen-bonded protons in octosilicate occupy relatively fixed positions, while the water molecules are relatively mobile.[28] This supports the mobility conclusions that have been made from this ^{1}H MAS spectrum.

Kanemite, magadiite and kenyaite also contain signals for strongly hydrogen-bonded protons and water molecules in their ^{1}H MAS spectra.[5,18] The lines are broader than those in octosilicate, and the informative spinning side-band manifolds are sometimes only seen after careful dehydration, but similar unambiguous assignments and conclusions confirming mobility can be made for these silicates.

Discussion

NMR studies reported here and elsewhere in the literature have shown clear inconsistencies which result when hypothetical structures for octosilicate, magadiite and kenyaite are constructed using makatite sheets as building blocks.

The first problem concerns the relationship between the $Q^3 : Q^4$ ratio, number of makatite sheets and layer widths of the resulting models. For example, Schwieger *et al.*,[4] Brandt *et al.*[17] and Nesbitt[1] based their magadiite models on $Q^3 : Q^4$ ratios of 1 : 2, 1 : 2 and 1 : 1.5, respectively. However, these values were obtained from spectra influenced by spin saturation. The measurements were taken from single-pulse spectra with recycle times of 120 s or less. For quantitative spectra, this delay must be of the order of five times the spin–lattice relaxation time. Dailey and Pinnavaia have since measured ^{29}Si T_1 values of 180 and 280 s for the Q^3 and Q^4 peaks, respectively, in magadiite, and used them to determine[9] a $Q^3 : Q^4$ ratio of 1 : 3. The makatite sheet based models[1,4,17] can be modified to reflect this more reliable $Q^3 : Q^4$ ratio by addition of extra makatite sheets, but this results in layers which are much too thick.

The second problem is highlighted by this work, and a recent study of ^{23}Na spectra of these silicates.[15] Table 3 compares data from ^{29}Si, ^{1}H and ^{23}Na NMR studies for the five layered sodium polysilicate hydrates, $KHSi_2O_5$ and piperazine silicate (EU19). Table 3 shows that makatite is not a good model for kanemite, octosilicate, magadiite and kenyaite. Where makatite has multiple Q^3 silicon atoms, no interlayer

Table 3 A review of useful structural information from X-ray diffraction and NMR spectroscopy for the five layered sodium polysilicate hydrates, $KHSi_2O_5$ and piperazine silicate (EU19)

	number of Q^3 silicon atoms		interlayer H-bonds		cations	
silicate	^{29}Si NMR	crystal structure	^1H NMR	crystal structure	number and type	method of deduction[a]
makatite	4	4	not observed	no	3 Na^+	(i) ^{23}Na DOR NMR (ii) crystal structure[b]
kanemite	1	—	observed	—	1 Na^+	^{23}Na NMR
octosilicate	1	—	observed	—	1 Na^+	(i) ^{23}Na NMR (ii) powder XRD
magadiite	1	—	observed	—	1 Na^+	^{23}Na NMR
kenyaite	1	—	observed	—	1 Na^+	^{23}Na NMR
$KHSi_2O_5$	1	1	observed	yes	1 K^+	crystal structure[c]
EU19	1	1	not observed	yes	1 $[pipz]^{2+}$	crystal structure[d]

[a] Ref. 15. [b] Ref. 3. [c] Ref. 21. [d] Ref. 20.

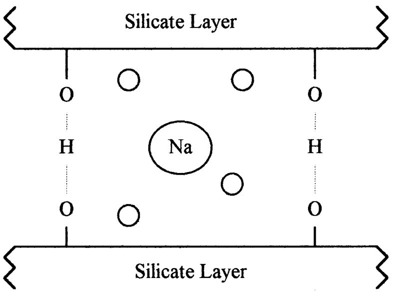

Fig. 8 A schematic diagram of a plausible interlayer space for kanemite, octosilicate, magadiite and kenyaite. Unfilled circles represent an indefinite number of water molecules.

hydrogen bonds and three types of sodium ion†, the other four layered sodium polysilicate hydrates have a single Q^3 silicon atom, interlayer hydrogen bonds and a single type of sodium ion. Allowing for the difference in counter ions, the latter are properties which are shared with $KHSi_2O_5$ and EU19. Therefore, from the parameters considered here, it can be concluded that $KHSi_2O_5$ and EU19 are better bases for forming model structures of kanemite, octosilicate, magadiite and kenyaite than makatite.

A plausible interlayer space for kanemite, octosilicate, magadiite and kenyaite can be formed by replacing the potassium ions of $KHSi_2O_5$ with hydrated sodium ions (Fig. 8). This would fit with all the data summarised in Table 3, as it includes a single type of Q^3 silicon atom, an interlayer hydrogen bond, and a single type of sodium ion. It would explain why the four silicates share common properties, such as ion exchange, and is consistent with any synthetic relationship between them. It fixes the position of the H-bonded proton and allows for mobile water molecules, which fits with the ^1H MAS spectra and ^{23}Na and ^{29}Si cross-polarisation behaviour discussed previously. It also allows for some speculation on the species surrounding the sodium ions in these silicates. Previous ^{23}Na NMR studies hinted that the coordination number of the sodium ions in kanemite might be five, while it is six in octosilicate, magadiite and kenyaite: second-order quadrupolar effects were significantly stronger in kanemite.[15] In kanemite, $NaHSi_2O_5{\cdot}3H_2O$, there are three water molecules per sodium ion, and for a pentacoordinate sodium ion we might propose dative bonding with three water-oxygen, $H_2\mathbf{O}$, atoms and two oxygen atoms from the silicate lattice, $\equiv Si-\mathbf{O}$. Octosilicate, $Na_2H_2Si_2O_{18}{\cdot}8H_2O$, has four water molecules per sodium ion and would again require two oxygen atoms from the silicate lattice for a hexacoordinate sodium ion. Magadiite and kenyaite, $Na_2H_2Si_xO_{2x+2}{\cdot}9H_2O$, have too much water for a hexacoordinate sodium ion formed in this way. This extra water, and any subsequent increase in the rate of exchange, would explain the broader lines that are seen in ^1H MAS spectra unless the silicates are dehydrated.

Discussion of $Q^3:Q^4$ ratios is complicated by two factors: (a) difficulties in determining the values accurately from ^{29}Si spectra because of the dangers of signal saturation, and (b) the variability of composition for different samples alluded to earlier (in some cases associated with adventitious sodium NaCl). The $Q^3:Q^4$ ratios given in Table 1 probably represent maximum (integral) values. An alternative way of discussing expected ratios can be based on a recognition that strong hydrogen bonding in kanemite (which contains only Q^3 silicon sites) may be associated with the presence of sodium ions, implying the existence of a $[NaHSi_2O_5]$ unit. If it is supposed that such a unit also exists for octosilicate, magadiite and kenyaite, these systems can ideally be formulated as:

octosilicate	$NaHSi_2O_5{\cdot}Si_2O_4{\cdot}4H_2O$
magadiite	$NaHSi_2O_5{\cdot}Si_5O_{10}{\cdot}4.5H_2O$
kenyaite	$NaHSi_2O_5{\cdot}Si_9O_{18}{\cdot}4.5H_2O$

Such a formulation suggests $Q^3:Q^4$ ratios of 1:1, 1:2.5, and 1:4.5, respectively, in agreement with the observed value for octosilicate and probably consistent with the measurements for the other two systems. Clearly, partial loss of sodium (or, alternatively, the presence of impurity NaCl), would cause variability in observed values. Our hypothesis regarding the $[NaHSi_2O_5]$ unit has the advantage of rationalising discussion of the structures. However, it may be noted that anion exchange has been observed for kanemite,[29] which implies the existence of OH^-, or perhaps of $[H-O\cdots H\cdots O-H]^-$. The latter has been observed in hydroxysodalite hydrate $[Na_4(H_3O_2)]_2[SiAlO_4]_6$ and gives NMR signals at $\delta \approx 16$ and $\delta \approx -1$.[30] For the layer silicates, signals at $\delta \approx -1$ have not been observed, though perhaps this is because of rapid exchange with other water protons.

In accordance with our suggestions, the ^{29}Si NMR spectrum of octosilicate has, indeed, two signals, Q^3 and Q^4, in a ratio of 1:1. It is a simpler spectrum than that of EU19 which has three signals, Q^3 and Q^4, in a ratio of 1:2. With EU19, each crystallographically distinct silicon atom has its own signal in the ^{29}Si NMR spectrum—there is no overlap. Since the lines in the octosilicate spectrum are sharp it is likely that we have no more than one distinct silicon atom of each connectivity in the structure of octosilicate. Therefore, the structure is likely to be simple, and a plausible model can be formed by simplifying the known EU19 structure, as shown in Fig. 9. This involves the hypothetical removal of one of the Q^4 silicon

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† Ref. 15 incorrectly refers to two sodium sites. However, two of the three sites have similar environments, so it may be said that there are two types of sodium site in makatite.

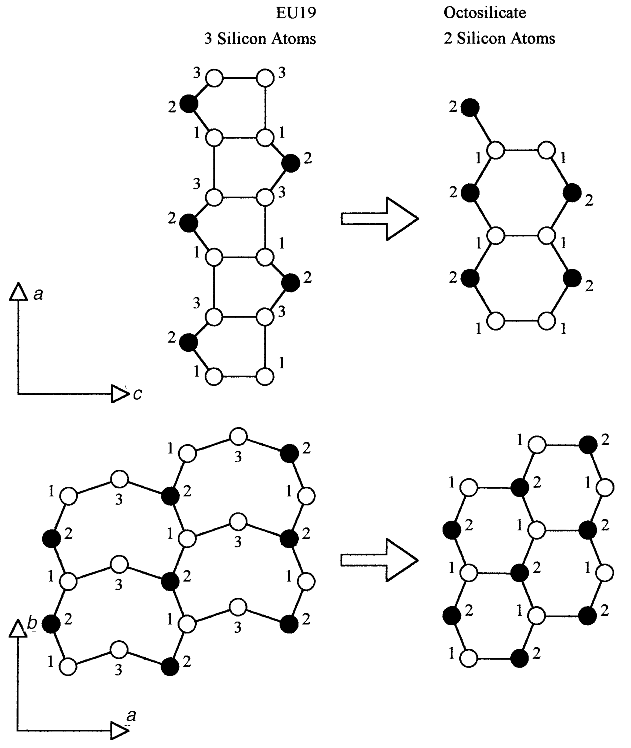

Fig. 9 The hypothetical modification of piperazine silicate (EU19) (three distinct silicon atoms, $Q^3:Q^4=1:2$) to give a plausible model for the silicate layer in octosilicate (two distinct silicon atoms, $Q^3:Q^4=1:1$). In each view of EU19 (shown on the left), silicon atom number 3 is removed. The schematic diagrams show silicon atoms as filled or unfilled circles, representing types Q^3 and Q^4 respectively.

atoms from EU19 to give a layer with two sheets of six-membered rings, connected by six-membered rings of silicon atoms. Alternatively, a double-sheet structure can be obtained by condensing two $KHSi_2O_5$ sheets, in the same way as previous authors have condensed makatite layers. This results in the structure depicted in Fig. 10, where two sheets of six-membered rings are connected by a combination of four- and eight-membered rings in one direction and six-membered rings in the other. Both silicate layers are plausible—they are simple, no thicker than the known basal spacing, correspond to a $Q^3:Q^4$ ratio of 1:1, and should be able to incorporate the interlayer space shown in Fig. 8. This is certainly the case for the second model, since the original conformation of hydrogen-bonded protons and alkali-metal ions need not change on condensing two $KHSi_2O_5$ sheets.

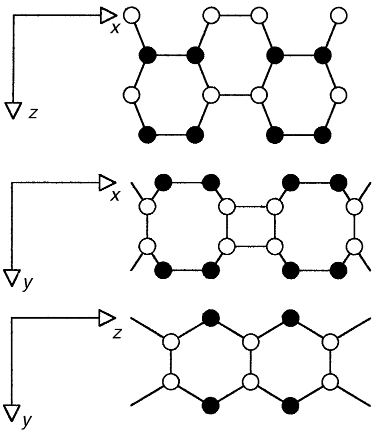

Fig. 10 Schematic diagrams of a plausible silicate layer for octosilicate formed by the hypothetical condensation of two $KHSi_2O_5$ sheets, showing silicon atoms as filled and unfilled circles, representing types Q^3 and Q^4, respectively

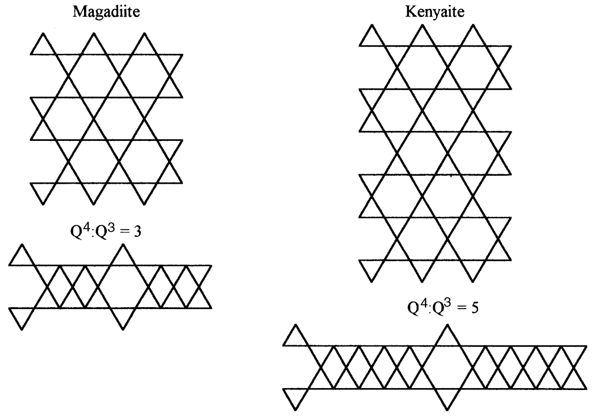

Fig. 11 Schematic diagrams of hypothetical silicate layer structures for magadiite and kenyaite. Triangles represent SiO_4 tetrahedra. The thicker layers could be made by condensing several octosilicate layers together, and the thinner layers by including more Q^4 silicon atoms in a double-sheet layer. This view would correspond to that along the x axis in Fig. 10.

These models of the octosilicate silicate layers must be modified to become plausible for magadiite and kenyaite: the degree of condensation must be increased to accommodate connectivity ratios of 1:3 and, probably, 1:5, respectively, while the thickness should remain consistent with the basal spacings indicated by powder X-ray diffraction. The simplest method of modifying the octosilicate structure thus is to make it thicker (*i.e.* with more sheets) but keep the arrangements of four-, six- and eight-membered rings, keeping the layer separation the same. Fig. 11 shows schematic representations for magadiite and kenyaite layers made in this way. They fit the accepted $Q^3:Q^4$ ratios, and explain why octosilicate, magadiite and kenyaite have similar interlayer spaces, but vary in basal spacing. However, they are too large: four- or six-sheet layers cannot be squeezed into a distance of 15 or 20 Å, respectively. An alternative would be to modify the octosilicate layer by including more Q^4 silicate atoms in each sheet. Fig. 11 shows that these models would fit the known $Q^3:Q^4$ ratios and are narrow enough. However, it is not easy to see why the basal spacings should increase so markedly in going from octosilicate to magadiite to kenyaite, unless there is severe puckering. Moreover, octosilicate, magadiite and kenyaite would no longer have the same interlayer space. Therefore, though simple plausible model structures can be formed for the octosilicate silicate layer, it is not possible to do the same for magadiite and kenyaite. This is understandable if the ^{29}Si NMR spectra are considered. All three silicates have a single Q^3 signal, corresponding to a common type of interlayer space, but the Q^4 regions of the relevant spectra (where signals are seen for silicate layer ^{29}Si nuclei) are very different. Octosilicate has a single Q^4 line, so a simple layer may be inferred. The ^{29}Si spectra of magadiite contains three lines, of non-uniform intensity,[9] and kenyaite ^{29}Si spectra tend to contain four Q^4 lines, though there is some variation in the literature.[1] Therefore, the silicate layers are likely to be fairly complex, with many slightly different silicon atoms making up the structure.

Conclusions

Previous authors[1,4] have tried to base model structures of kanemite, magadiite, octosilicate and kenyaite on the known structure of makatite.[3] This work has highlighted significant differences in the ^{29}Si and ^{1}H NMR spectra of makatite and the other four layered sodium polysilicate hydrates concerning the presence of multiple Q^3 silicon signals and strongly hydrogen-bonded protons. When ^{23}Na NMR information is also considered, it becomes clear that better models of kanemite, octosilicate, magadiite and kenyaite may be based on the known structure of the anhydrous potassium disilicate, $KHSi_2O_5$. An interlayer space formed in this way includes hydrogen-bonded protons and a single type of Q^3 silicon atom, as well as being consistent with proton-mobility conclusions from ^{1}H MAS NMR or ^{29}Si and ^{23}Na cross-polarisation NMR experiments, possibly even accommodating sodium coordination number proposals from ^{23}Na NMR studies.

Conclusions can also be made regarding the silicate layers of these systems. Apperley *et al.* have already reported that the structure of kanemite is probably similar to that of $KHSi_2O_5$.[5] Simple structures can be proposed for octosilicate on the basis of NMR spectra which indicate the presence of a small number of silicon environments: one of type Q^3 and one of type Q^4. Plausible models can be formed by modifying the known structure of piperazine silicate (EU19) or by the condensation of $KHSi_2O_5$ silicate sheets. Similar models are less successful in describing the silicate layers in magadiite and kenyaite, where the ^{29}Si NMR spectra are more complicated. This must not be considered a failure of the ideas behind this work because the plausibility of the interlayer space models are unaffected. If the silicates are to find industrial uses, it is these interlayer species which will govern the properties, so the most important part of the structural elucidation is contained there.

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